Indian J. Phys. **71B** (1), 69–79 (1997)

IJP B
- an international journal

Vibrational spectral studies and thermodynamic functions of 5-carbethoxy-2-thiouracil

Vir Singh, Seema*, B S Yadav+ and Subhash Chand++
Molecular Spectroscopy and Biophysics Laboratory, Department of Physics, D N (P G) College, Meerut-250 002, India

Received 29 November 1995 accepted 16 September 1996

Abstract : The infrared and Raman spectra of solid 5-carbethoxy-2-thiouracil have been reported. The tautomeric forms and hydrogen bonding are also discussed The assignments of fundamental frequencies to various modes of vibration have been proposed. The thermodynamic functions *viz* enthalpy, free energy, heat capacity and entropy, have also been calculated using the experimental frequencies of infrared and Raman spectra of the said molecule

Keywords : Infrared and Raman spectroscopy, vibrational frequencies of carbethoxy thiouracil, thermodynamic functions

PACS Nos. : 33.20.Ea, 33.20 Fb

1. Introduction

The N-hetrocyclic molecules such as pyrimidine, cytocine, uracil and their derivatives are of immense importance, because some of them are the basic constituents of DNA and RNA and play an important role in constitution properties of nucleic acids [1–8]. Recent spectroscopic studies [1,2] of uracil and its derivatives have been motivated by their biological importance. A complete study [9] of vibrational spectra of 5-carbethoxy-2-thiouracil has not been made so far, hence the present investigations were undertaken to study the vibrational spectra, hydrogen bonding, tautomeric behaviour and thermodynamic functions of 5-carbethoxy-2-thiouracil and to identify the frequencies of different modes of vibration in this molecule.

*To whom all correspondence should be made
++Department of Chemistry, Meerut College, Meerut-250 002, India
+Department of Chemistry, J. V. (P. G.) College, Baraut, Meerut-250 002, India

2. Experimental

Spec-Pure grade sample of 5-carbethoxy-2-thiouracil (hereafter referred as 5,2-CETU) was obtained from M/S Aldrich-Chemie, West Germany and its purity was confirmed by elemental analysis and melting point determination. Infrared (i.r.) spectrum of the above molecule was recorded on Perkin-Elmer M 683 Spectrophotometer in the region 200–4000 cm^{-1} in KBr pellet and polythene film, while laser Raman spectrum was recorded on Spex-Ramalab Spectrophotometer using 52 MG Argon-Krypton laser of wavelength 488 nm.

3. Results and discussion

The vibrational spectra (Infrared and Raman) of 5,2-CETU have been shown in Figures 1 and 2. The observed fundamental frequencies alongwith their assignments are given in Table 1. The tautomerism and tautomeric forms of neutral, cationic and anionic forms are

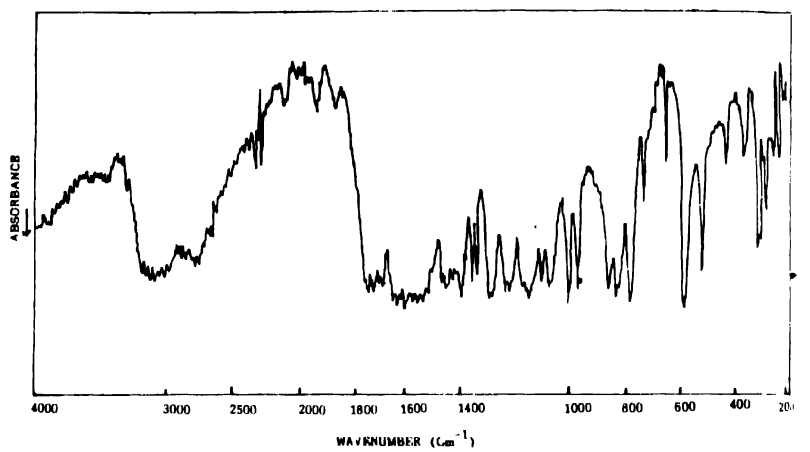


Figure 1. Infrared absorption spectrum of 5,2-CETU

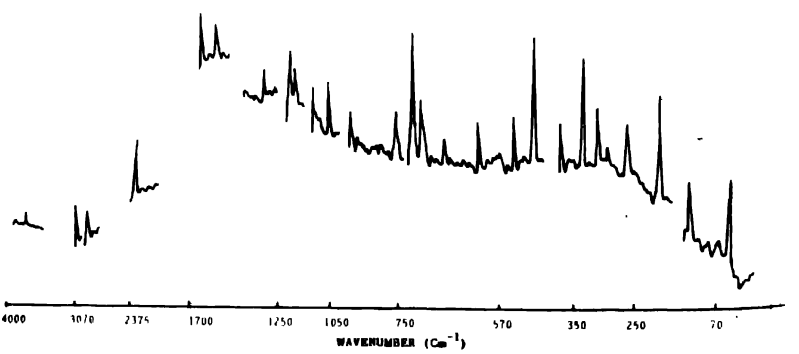


Figure 2. Laser Raman spectrum of 5,2-CETU

Table 1. Assignments of infrared and Raman spectra of 5-carbethoxy-2-thiouracil

IR bands	[All values in cm^{-1}] Raman bands	Assignments
3290 w		ν (N–H)
3060 w	3070 w	ν (N–H)
3020 w	3010 w	ν (C–H)
2980 w		ν_{asym} (CH_3)
2930 mw		ν_{asym} (CH_2)
2920 m		ν_{sym} (CH_3)
2880 m		ν_{sym} (CH_2)
2360 w	2375 w	ν (S–H)
1730 m	1735 ms	ν (C_5=O_2)
1700 m	1705 w	ν (C_2=O_1)
1630 w	1630 s	ν (C_3=C_4)
1570 m	–	β (N–H)
1535 m	1520 m	ν (C–N)
1500 w	–	ν (C–N)
1480 ms	1490 m	β_{asym} (CH_3)
1460 w	–	ν_{ring}
1450 w	–	β (C–H)
1440 w	–	β_{sym} (CH_2)
1410 w	–	β_{sym} (CH_3)
1370 vs	–	γ_{sym} (CH_2)
1350 vs	–	ν_{ring}
1230 vw	1240 m	ν_{ring}
1160 vw	–	ν (C=S)
1110 m	–	ν_{asym} (O–C–C)
1080 vw	1070 s	ν_{ring}
1040 w	1040 m	CH_3 rocking
1010 vs	–	β_{ring}
975 vs	–	γ (N–H)
930 m	925 w	ν_{sym} (O–C–C)
865 s	850 m	γ (N–H)
840 s	–	ν (C–H)
790 vs	–	CH_2 rocking, γ ring
750 w	750 vs	β_{sym} (CH_2)
735 vs	–	β (C=O)
680 vw	680 w	ν (C–S)
650 vs	–	β_{ring}
635 vw	635 w	β (C=S)
590 vs	575 s	γ_{ring}, β (C–H)
525 vs	540 vs	β_{ring}, β (C=O)
450 w	–	γ (C=O)
390 m	395 w	γ (C=O)

Table 1. *(Cont'd.)*

IR bands	[All values in cm^{-1}] Raman bands	Assignments
350 w	365 vs	β (C–CH_3)
320 m	320 m	β (C–S)
310 m	–	β (O–C–C)
285 vs	280 m	γ (C=S)
230 vs	235 vs	γ (C–N)
215 ms	–	(O–CH_2) torsion
	115 m	SH torsion

w = Weak, vw = Very weak, m = Medium, ms = Medium strong, mw = Medium weak, s = Strong, v s = Very strong, ν = Stretching, ν_{sym} = Symmetric stretching, ν_{asym} = Asymmetric stretching, β = In-plane-bending, β_{asym} = Symmetric in-plane bending, β_{asym} = Asymmetric in-plane bending, γ= Out-of-plane bending, γ_{sym} = Symmetric out-of-plane bending

presented in Figures 3 and 4 respectively. The inter and intramolecular hydrogen bonding of the said molecule have been shown in Figure 5.

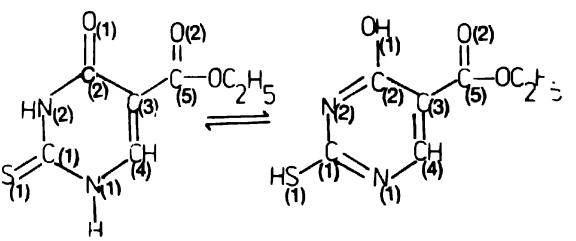
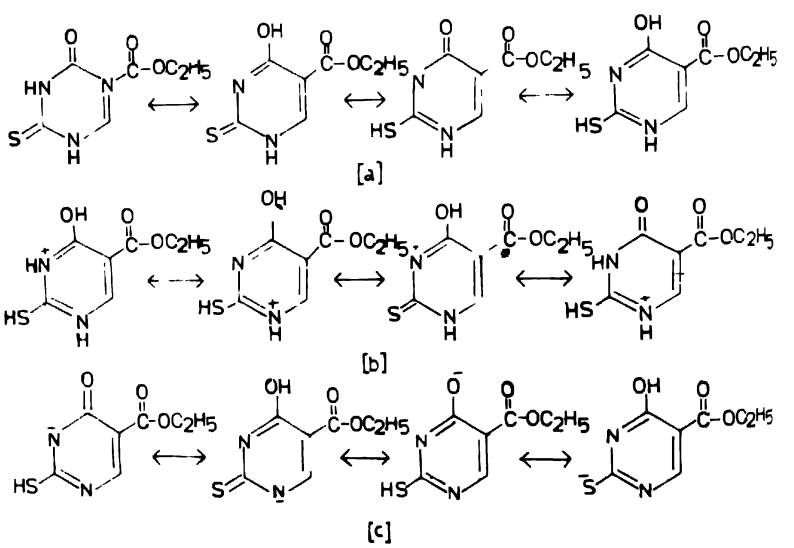


Figure 3. Tautomerism In 5-carbethoxy-2-thiouracil



The statistically computed thermodynamic functions *viz.* enthalpy function, free energy function, entropy and heat capacity with absolute temperature are given in Table 2

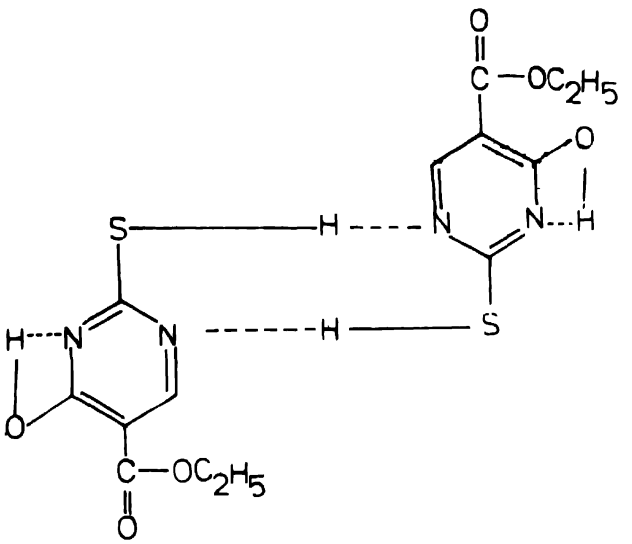


Figure 5. Inter and intramolecular hydrogen bonding in 5-carbethoxy-2-thiouracil.

Table 2. Thermodynamic functions (in cal/mole-°K) of 5,2-CETU.

Temperature (°K)	$\frac{H^o - E_o^o}{T}$	$\frac{F^o - E_o^o}{T}$	S^o	C_p^o
200	13.20	61.93	75.13	21.84
273	16.40	66.82	83.22	28.37
300	17.58	68.51	86.09	30.60
400	27.78	74.44	96.22	37.91
500	25.61	79.96	105.56	43.77
600	29.04	85.10	114.15	48.39
700	32.07	89.96	122.04	52.03
800	34.76	94.56	129.32	54.93
900	37.13	98.91	136.05	57.27
1000	39.24	103.04	142.29	59 17
1100	41.13	106.97	148.10	60.74
1200	42.82	110.70	153.53	62.04
1300	44.34	114.27	158.62	63.13
1400	45.72	117.68	163.41	64.06
1500	46.97	120.95	167.92	64.84

$\frac{H^o - E_o^o}{T}$—Enthalpy function, S^o—Entropy function,

$\frac{F^o - E_o^o}{T}$—Free Energy function, C_p^o—Heat capacity function,

where H^o, F^o and E_o^o are enthalpy, free energy and zero point energy respectively.

for the above molecule. The variation of enthalpy and heat capacity with absolute temperature is shown in Figure 6 while the variation of free energy and entropy with

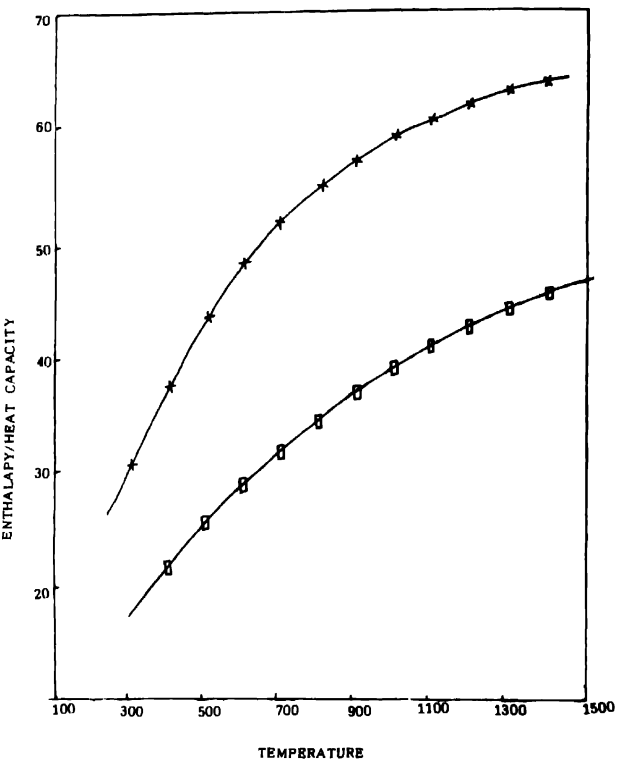


Figure 6. Temperature *vs* enthalpy / heat capacity 5,2-CETU
□ Enthalpy, × Heat capacity.

absolute temperature is shown in Figure 7. The molecular structure of 5,2-CETU is shown in Figure 8.

Vibrational spectra :

The interpretations are based on the assumption of the point group C_s for the molecule 5,2-CETU and the observed fundamentals have been assigned to different normal modes of vibration. The analysis of the bands and the assignments of the fundamental frequencies are made with the help of the assignment made by earlier workers in the similar molecules.

A. Ring vibrations :

(N–H, C–H, C–C and C–N vibrations)

The molecule under present investigation is tri-substituted uracil, therefore, only one C–H valance oscillation is expected. The C–H stretching value has been calculated for

uracil at 3065 cm^{-1} [10]. In view of this, the weak Raman band at 3010 cm^{-1} with its i.r. counterpart at 3020 cm^{-1} in 5,2-CETU has been assigned to the C–H vibration which is also in accordance with the literature value [7].

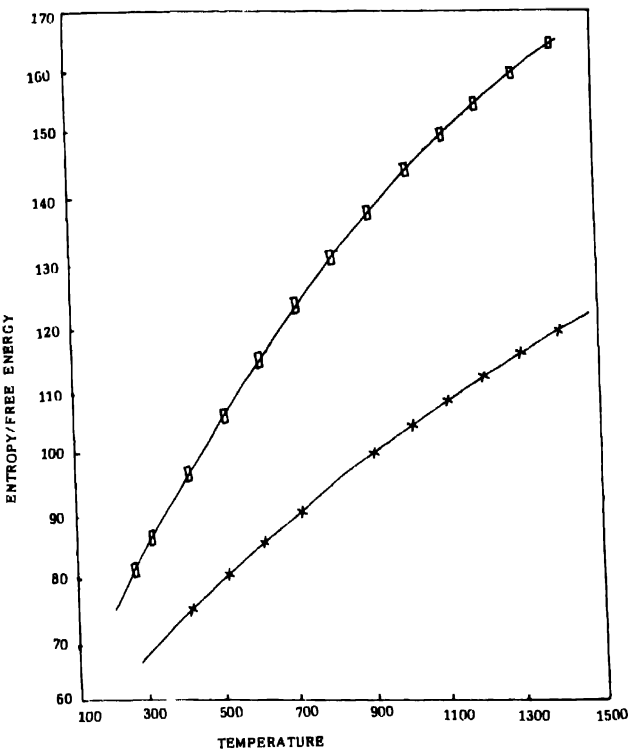


Figure 7. Temperature *vs* entropy / free energy 5-carbethoxy-2-thio-uracil.
□ Entropy, × Free energy

The frequency region for N–H stretching vibration has also been calculated in uracil [8,11]. In accordance with it i.r. bands at 3290 cm^{-1} and at 3060 cm^{-1} alongwith the Raman band at 3075 cm^{-1} are assigned to N–H stretching modes.

The band observed at 1450 cm^{-1} in this molecule, has been assigned to C–H in-plane-bending mode. It has been stated that in uracil, the higher wave number band at 850 cm^{-1} is N–H out-of-plane bending mode while the lower wave number band at 805 cm^{-1} is in-plane-bending vibration [9].

During the present study, the strong i.r. band observed at 865 cm^{-1} has been taken to represent N–H out-of-plane bending mode while no band is observed around 805 cm^{-1}. The strong band in i.r. spectrum at 840 cm^{-1} with counterpart of Raman band at 850 cm^{-1} is assigned to C–H out-of-plane bending mode in the said molecule, which find support from

the work available in the literature [7,8]. It has been identified that the C–N in-plane-bending vibration exists at 1054 cm^{-1} in 5,6-dimethyl uracil [12]. This mode has been assigned at 1010 cm^{-1} in 5,2-CETU.

B. C–X Vibrations :

In 5,2-CETU only $C_2=O_1$ and $C_3=C_4$ double bonds are present and a thio-group is present at position 2. Sanyal *et al* [13,14] have assigned these vibrations at 1690, 1676 and 1614 cm^{-1} respectively. Out of the three, the two bands at 1700 and 1630 cm^{-1} in i.r. spectrum are assigned to $C_2=O_1$ and $C_3=C_4$ stretching fundamentals alongwith the Raman values at 1705 and 1630 cm^{-1} respectively.

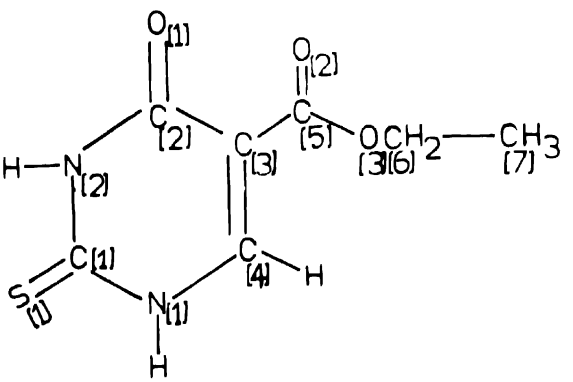


Figure 8. Molecular structure of 5,2-CETU

The C–S stretching frequencies generally appears in the region 720-570 cm^{-1} [15] while this frequency has been observed at 689 cm^{-1} in methyl phenyl sulphide [16]. In this accordance, a weak i.r. band at 680 cm^{-1} with counterpart of Raman band at 680 cm^{-1}, in 5, 2-CETU has been taken to represent this mode. The C=S stretching band is assigned at 1160 cm^{-1} in the same molecule, which find support from the literature value [16].

C. Group vibration :

(i) SH group :

Bellamy [17] has suggested the range 2290–2550 cm^{-1} for SH stretching mode and proposed that the band near 2550 cm^{-1} in thiophenols were absent in their corresponding sulphides which makes it evident that this band is due to SH stretching mode. A weak i.r. band at 2360 cm^{-1} with counter part of Raman band at 2375 cm^{-1} in 5,2-CETU has been observed which is assigned to SH stretching vibrations supported by the literature values [17]. It has been proposed that the –SH torsion occurs at 137 cm^{-1} in benzyl mercaptan [18]. In this accordance, the Raman band at 115 cm^{-1} in 5,2-CETU has been taken to represent –SH torsional band.

(ii) $-\overset{O}{\overset{\|}{C}}-OCH_2-CH_3$ group :

In the present molecule, carbethoxy group contained CH_3, O–CH_2, C=O *etc.* groups. It has been assigned that the symmetric and asymmetric CH_3 stretching modes occur at 2872 cm^{-1} and 2962 cm^{-1} respectively [19]. The weak i.r. bands at 2980 and 2920 cm^{-1} in 5,2-CETU have been assigned to CH_3 asymmetrical and symmetrical stretching modes respectively. It has also been assigned that –CH_2 asymmetric and symmetric stretching bands occur at 2926 and 2853 cm^{-1} respectively [17] while we have assigned the i.r. band at 2930 and 2880 cm^{-1} to the CH_2 asymmetric and symmetric modes respectively. The CH_3 out-of-plane bending mode have been assigned at 1040 cm^{-1} in the title compound in accordance with earlier workers [20].

It was suggested that all the carbonyl frequencies of alkyl esters absorb between 1748 and 1730 cm^{-1} in carbon tetrachloride solution [17]. In carbethoxy group a medium intensity band at 1730 cm^{-1} has been assigned to $C_5=O_2$ stretching vibration in our study. It has been assigned that O–CH_2 torsion at 220 cm^{-1} occurs in isomeric ethoxy benzonitriles [21] In this accordance, Raman band at 215 cm^{-1} has been assigned to O–CH_2 torsion in 5, 2-CETU.

Hydrogen bonding and tautomeric behaviour :

The bands observed in i.r. spectrum of 1-methyl uracil in the region 3100 to 2800 cm^{-1} are due to hydrogen bonded NH stretching frequencies [22]. This supports the assignment of bands observed in the region (Table 1) during the present study. The presence of additional NH stretching modes is due to the strong inter molecular and intramolecular association [22,23]. The presence of C=S stretching and C=S bending modes in the compound, indicate that H atom of –SH group is migrating to the N atom of the ring, but at the same time, existence of C–S band stretching mode shows that migration of H atom from –SH group is not complete. Therefore, the H atom is simultaneously associated with both sulphur and nitrogen.

The band at 1673 cm^{-1} in uracil is assigned as ($C_2=O_1$) mode [8]. Thus, the band at 1700 cm^{-1} in 5,2-CETU corresponds to this vibration. Hence it is concluded that in 5,2-CETU, the hydroxyl group present at position 4 is in cationic form and its H atom has moved to N_2 of the ring showing tautomerism in the molecule as shown in Figure 3. However, at the same time, the presence of a weak OH stretching mode similarly indicates that migration of H atom of OH group is not complete. The presence of the said OH stretching mode further suggests that the -OH group is involved in hydrogen bonding. Uracil, due to the presence of two C=O groups at position 2 and 4 and two NH groups at 1 and 3, generally tautomerises to give a hydroxy aromatic compound. But in 5,2-CETU, only one $C_2=O_1$ group is present at position 4, as there is a $C_1=S_1$ group at position 2. This compound will, therefore, tautomerise to give a monohydroxy compound *viz.* 5-carbethoxy-4-hydroxy-2-mercapto pyrimidine. The neutral, cationic and anionic tautomeric forms of the said compound are shown in Figure 4.

Thermodynamic functions :

The thermodynamic functions *viz.* enthalpy function, heat capacity, free energy function and entropy of the molecule 5,2-CETU, have been computed using the standard expressions [24]. We take *Y*-axis perpendicular to the molecular plane and *Z*-axis to pass through the paraposition. The following structural parameters of the said molecule are used [25,26].

Bond length (Å)		Bond angle (degree)	
C_1–N_1	1.33	$\measuredangle N_1C_1S_1$	122°
C_1–N_2	1.33	$\measuredangle N_2C_1S_1$	122°
N_2–C_2	1.40	$\measuredangle N_2C_2O_1$	118°
C_2–C_3	1.45	$\measuredangle C_3C_2O_1$	126°
C_3–C_4	1.35	$\measuredangle C_5C_3C_2$	117°
C_4–N_1	1.33	$\measuredangle C_5C_3C_4$	124°
C_1–S_1	1.65	$\measuredangle C_3C_5O_2$	120°
C_2–O_1	1.28	$\measuredangle O_2C_5O_3$	126°
C_3–C_5	1.59	$\measuredangle O_3C_5C_3$	124°
C_5–O_2	1.21	$\measuredangle C_2C_3C_4$	116°
C_5–O_3	1.21		
C_6–C_7	1.49		

All other angles were taken as 120° of the ring. The thermodynamic functions have been calculated at different temperatures between 200–1500°K using 30 fundamental frequencies [Assuming N_1H, C_2, O_2, C_1, S_1, N_2H, O_1, C_3, C_4H, C_5, $O_3C_6H_2$ and C_7H_3 as single atoms]. Hence, 12 atoms are considered in the present compound (Figure 8) assuming rigid rotator harmonic oscillator approximation.

The calculation were performed for one mole of an ideal gas at one atmospheric pressure. The symmetry number for overall rotation is 2. The principal moment of intertia were found to be 212.54, 260.46 and 47.91 × 10^{-39} gm-cm^2 in 5,2-CETU, while reduced moment of intertia is 10.52.

The variation of enthalpy, heat capacity, free energy and entropy with absolute temperature are in agreement with the trend reported in the literature [27].

References

[1] V K Rastogi, H P Mittal, Y C Sharma and S N Sharma *Spectroscopy of Biological Molecules* eds R E Hester and R B Girling (London . Royal Soc of Chemistry) p 403 (1991)

[2] V K Rastogi, S Arora, S L Gupta and D K Sharma *Spectroscopy of Biological Molecules* eds R E Hester and R B Girling (London . Royal Soc. of Chemistry) p 401 (1991)

[3] J Bandekar and G Zundel *Spectrochim. Acta* **39A** 343 (1983)

[4] Y B Singh, A S Khan and Uday Bhanu *Indian J Chem.* **26A** 1066 (1987)

[5] R A Yadav, P N S Yadav and J S Yadav *Proc. Indian Acad. Sci.* **69** 100 (1988)

[6] S Aruna and Shanmugam *Spectrochim. Acta* **38A** 815 (1985)

[7] L Harsanyi and P Csaszar *Acta Chim. Hung.* **113** 257 (1983)

[8] A J Barnes, M A Stuckey and L Le Gall *Spectrochim. Acta* **40A** 419 (1984)

[9] J Bandekar and G Zundel *Spectrochim. Acta* **38A** 815 (1982)

[10] Y Nishimura, M Isuboi, S Kato and K Morokuma *J. Am. Chem. Soc.* **103** 1354 (1981)

[11] B S Yadav, S D Sharma, Seema and Vibha Sharma *Asian J. Phys.* **3** 229 (1994)

[12] R K Goel, S K Gupta, M L Agarwal and S N Sharma *Indian J. Pure Appl. Phys.* **19** 501 (1981)

[13] N K Sanyal, S L Srivastava and D N Verma *Indian J. Phys.* **50** 865 (1976)

[14] N K Sanyal, S L Srivastava and R K Goel *Indian J. Phys.* **52B** 108 (1977)

[15] C N R Rao *Chemical Applications of Infrared Spectroscopy* (New York : Academic) (1963)

[16] J H S Green *Spectrochim. Acta* **24A** 1627 (1968)

[17] L J Bellamy *Infrared Spectra of Complex Molecules* (London : Chapman and Hall) p 395 (1975)

[18] P K Mallick, S Chattopadhyaya and S B Banerjee *Indian J. Pure Appl. Phys.* **11** 609 (1973)

[19] Fox and Martin *Proc. Roy Soc.* **175** 208 (1940)

[20] J K Wilmshurst and H J Bernstein *Can. J. Chem.* **35** 911 (1957)

[21] A M Joshi, K Rao Suryanarayana and M A Shashidhar *Indian J. Pure Appl Phys* **28** 527 (1990)

[22] M Szczesniak, M J Nowak, K Szczesniak and W B Person *Spectrochim. Acta* **41A** 237 (1985)

[23] D G O Sullivan and P W Sadler *J. Chem. Soc.* 876 (1959)

[24] G Herzberg *Molecular Spectra and Molecular Structure Vol II Infrared and Raman Spectra* (N J . Princeton D Van Nostrand) p 511 (1996)

[25] C L Chatterjee, P P Garg and R M P Jaiswal *Spectrochim. Acta* **34A** 943 (1978)

[26] R K Goel and M L Agarwal *J. De Chim. Phys* **79** 765 (1982)

[27] B S Yadav *PhD Thesis* (Meerut University, Meerut, India) (1991)